γ-Radiolysis of Aqueous Solutions of Tellurium

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γ-Radiolysis of Aqueous Solutions of Tellurium

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Radiation induced reactions of Te(IV) and Te(VI) compounds labelled with ^{132}Te and ^{123m}Te respectively, in deaerated 0.4 M H_2SO_4 or HNO_3 solution, were investigated by the use of a ^{60}Co γ-ray source. The yield of radiation induced oxidation of Te(IV) and that of reduction of Te(VI) were very small and increased in proportion to their concentrations. Based on the reaction mechanism proposed by M. Haissinsky *et al.*, who had shown that almost all the OH and H radicals reacted with the stable radiolytic products (H_2O_2, H_2, O_2) to yield water, the dependence of the yield of oxidation or deduction on the concentrations of tellurium compounds was elucidated quantitatively. The rate constant of the reaction Te(VI)+H was estimated to be about 5×10^6 M^{-1} sec.$^{-1}$

I. INTRODUCTION

γ-Radiolysis of Te(IV) or Te(VI)** in 0.4 M H_2SO_4 solutions was investigated by M. Haissinsky *et al.*[1] and the following mechanism was proposed:

$$H_2O \rightsquigarrow H,\ OH,\ H_2,\ H_2O_2, \qquad (0)$$

$$Te(IV)+OH \longrightarrow Te(V), \qquad (1)$$

$$2Te(V) \longrightarrow Te(IV)+Te(VI), \qquad (1')$$

$$Te(VI)+H \longrightarrow Te(V), \qquad (2)$$

$$Te(IV)+HO_2 \longrightarrow Te(VI)+OH, \qquad (3)$$

$$2HO_2 \longrightarrow H_2O_2+O_2, \qquad (4)$$

$$H+O_2 \longrightarrow HO_2, \qquad (5)$$

$$H_2O_2+H \longrightarrow H_2O+OH, \qquad (6)$$

$$H_2O_2+OH \longrightarrow H_2O+HO_2, \qquad (7)$$

$$H_2+OH \longrightarrow H_2O+H. \qquad (8)$$

Since several competing reactions can occur at the same time, the kinetics of the overall process is complex and depends on the chemical atmosphere. For example, in the absence of oxygen, the reduction of Te(VI) (reaction (2)) can compete effectively with the oxidation of Te(IV) (reaction (1)). Therefore, it is desirable to investigate in detail the overall kinetics with Te(IV) and Te(VI) labelled with respective tracers.

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** Te(IV) is probably present as a mixture of H_2TeO_3 and $HTeO_2^+$ in acid solution and Te(VI) is as a mixture of H_6TeO_6 and H_2TeO_4.[3] For simplification we denote as Te(IV) and Te(VI).

In this paper, the radiation induced reactions of tellurium compounds in deaerated 0.4 M H_2SO_4 or HNO_3 solutions are investigated and the results are explained by the mechanism proposed by M. Haissinsky *et al.*[1]

II. EXPERIMENTAL

^{132}Te(half life: 78 h) was separated from fission products and ^{123m}Te (half life: 117 d) was produced by irradiating natural tellurium at the Kyoto University Reactor. Te(IV) labelled with ^{132}Te (~1 mCi/g) and Te(VI) labelled with ^{123m}Te (~1 mCi/g) were prepared.[2] The concentrations of Te(IV) and Te(VI) in 0.4 M H_2SO_4 or HNO_3 solutions are shown in table I. Sample solutions were deaerated with nitrogen gas for about two hours, were sealed in quartz tubes and were then irradiated with γ-ray at the ^{60}Co γ-ray irradiation facility of the Institute for Chemical Research, Kyoto University. The dose rate was kept constant at 6.5×10^4 rad/h.

After irradiation, the sample solution was transferred into 10 ml of 6 M HCl containing each 10 mg of Te(IV) and Te(VI) carriers. The solution was passed through an ion-exchange column (2 cm$\phi\times$5 cm) containing Dowex-1X8 (RCl, 100~200 mesh) and the column was washed with several free volumes of HCl solution of the same concentration. Te(VI), which passed through the column, was reduced to the metallic form by boiling the solution with hydrazine hydrochloride and $NaHSO_3$. Te(IV) absorbed in the column was eluted with 20 ml of 0.1 M HCl solution and was reduced to the metallic form by $NaHSO_3$. The chemical yields of Te(IV) and Te(VI) were found to be 80~90 %.

The 159 KeV γ-ray associated with ^{123m}Te and the 228 KeV γ-ray associated with ^{132}Te were analysed with a 54 cm^3 Ge(Li) detector connected to 400 ch. PHA, and the amounts of oxidation of Te(IV) and those of reduction of Te(VI) were obtained.

III. RESULTS AND DISCUSSION

Both the amounts of oxidation of Te(IV) and those of reduction of Te(VI) induced by radiation were proportional to the absorbed dose (1×10^5~5×10^5 rad). Table I shows the yields of oxidation of Te(IV) and reduction of Te(VI) (G(Te(VI)) and G(Te(IV))). It was testified at the same time that there was no exchange reaction between Te(IV) and Te(VI) in the unirradiated samples.

From the table, we can draw two conclusions: (A) compared with the well known yields of OH radicals and H atoms in acid solution ($g_{OH}=2.96$, $g_H=3.68$[4]), the observed yields of oxidation and reduction of tellurium compounds are very low, and (B) the yields increase in proportion to their own concentrations as shown in Figs. 1 and 2.

The predominent reactions in H_2SO_4 solutions must be those with the stable radiolytic products (H_2O_2, H_2, O_2) (reactions (4) to (8)), since SO_4^{2-} ion is not reactive. In HNO_3 solutions, on the other hand, H atoms also react with NO_3^- ions following the reaction:

$$H+NO_3^- \longrightarrow NO_2+OH^- . \qquad (9)$$

It was shown in Fig. 2 that the yield of reduction in the HNO_3 solution is much lower than that in the H_2SO_4 solution.

Table I. The Yields of Oxidation and Reduction of Tellurium Compounds in 0.4 M H_2SO_4 or HNO_3 Solution

Sample	[Te (IV)]	[Te (VI)]	G(Te (VI))	G(Te (IV))
H_2SO_4–1	2.1 (10^{-4}M)	4.5 (10^{-4}M)	0.070	0.066
2	2.3	2.3	0.066	0.036
3	2.1	1.2	0.059	0.017
4	2.3	0.5	0.056	0.007
5	1.3	4.3	0.045	0.064
6	0.5	4.7	0.030	0.063
7	0.2	4.8	0.008	0.061
HNO_3–1	2.1	2.9	0.040	0.020
2	2.0	1.9	0.040	0.013
3	2.0	0.8	0.041	0.006
4	2.1	0.2	0.040	0.002
5	1.1	3.4	0.029	0.040
6	0.5	3.9	0.013	0.040
7	0.3	4.0	0.010	0.030

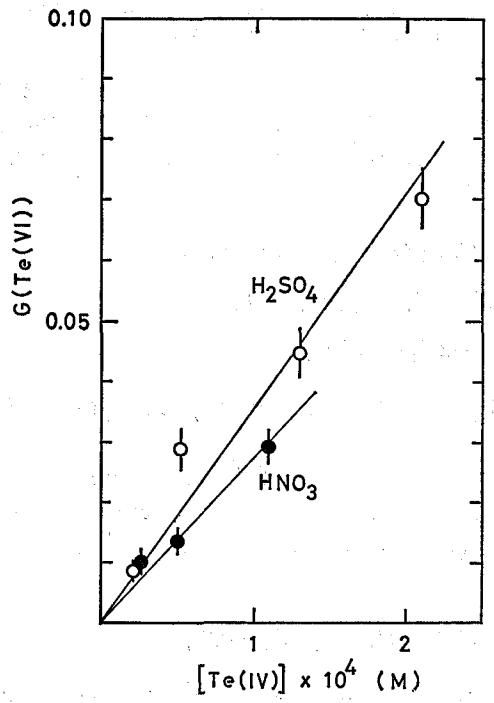

Fig. 1. The yield of oxidation G(Te(VI)) *vs.* [Te(IV)]. [Te(VI)] is kept constant at $\sim 4\times10^{-4}$ M and [H_2SO_4] or [HNO_3] is 0.4 M.

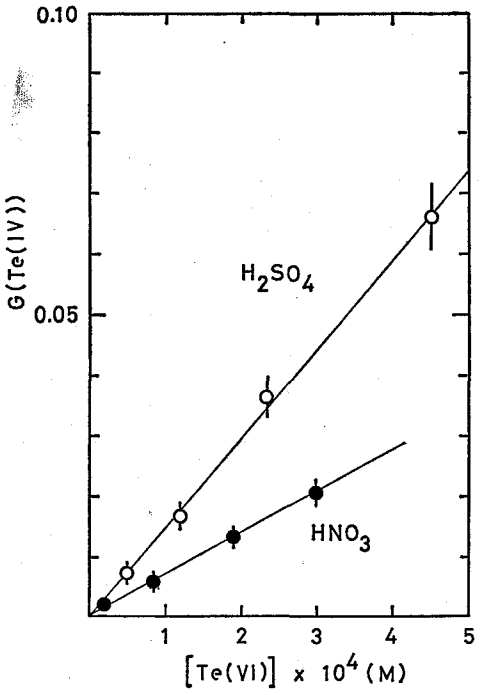

Fig. 2. The yield of reduction G(Te(IV)) *vs.* [Te(VI)]. [Te(IV)] is kept constant at $\sim 2\times 10^{-4}$ M and [H_2SO_4] or [HNO_3] is 0.4 M.

Since the yields of reactions (1)$\sim$(3) are negligibly small, application of stationary state kinetics in H_2SO_4 solution to OH, H, and HO_2 radicals leads to the following equations:

$$G(\mathrm{OH}) = 2.96+G_6-G_7-G_8 = 0\,, \qquad (\mathrm{I})$$

$$G(\mathrm{H}) = 3.68-G_5-G_6+G_8 = 0\,, \qquad (\mathrm{II})$$

$$G(\mathrm{HO_2}) = -2G_4+G_5+G_7 = 0\,, \qquad (\mathrm{III})$$

where the values 2.96 and 3.68 are the primary radiolytic yields of OH and H radicals, respectively.[4]

$G(H_2O_2)$ was found to be about 0.3 in the sample H_2SO_4-1. This yield is nearly equal to that measured by M. Haissinsky *et al.* in a deaerated solution containing 5×10^{-4} M Te(IV) or 5×10^{-4} M Te(VI).[1] We can get the following equation:

$$G(\mathrm{H_2O_2}) = 0.81+G_4-G_6-G_7\simeq 0.3\,, \qquad (\mathrm{IV})$$

where the value 0.81 is the primary radiolytic yield of H_2O_2[4]. As the rate constant k_5 is known to be large enough to permit stationary state kinetics on oxygen ($k_5=1.2\times 10^{10}\,\mathrm{M^{-1}\,sec^{-1}}$),[5] we can also get the following equation:

$$G(O_2) = G_4 - G_5 \simeq 0 . \qquad (V)$$

Combining equations (I) to (V), we obtain the following reaction yields:

$$G_4 \simeq G_5 \simeq G_7 \simeq 3.32 ,$$
$$G_6 \simeq 0.51, \quad G_8 \simeq 0.15 . \qquad (VI)$$

It is of interest that one can estimate the rate constant k_2 using the obtained reaction yields G_2 and G_6. We can write:

$$\frac{G_2}{G_6} = \frac{2G(\mathrm{Te(IV)})}{G_6} = \frac{k_2[\mathrm{Te(VI)}]}{k_6[H_2O_2]} .$$

From the mean value of $[H_2O_2]$ in the irradiation of about 1×10^{-4} M combined with the value of $G(\mathrm{Te(IV)})/[\mathrm{Te(VI)}] = 1.5 \times 10^2$ obtained from Fig. 2, with $G_6 \simeq 0.51$ and with $k_6 = 9 \times 10^7\ \mathrm{M^{-1}\,sec.^{-1}}$ [6] we can get:

$$k_2 \simeq 5 \times 10^6\ \mathrm{M^{-1}\,sec.^{-1}}$$

Because the concentration of hydrogen peroxide could not be measured accurately and because several approximations were included in the deduction, the value of k_2 thus obtained is tentative. However, this value is significantly lower than that of $1.05 \times 10^8\ \mathrm{M^{-1}\,sec^{-1}}$ found by M. Haissinsky *et al.*[1] Their value G_2 obtained indirectly from observing $G_2 - G_1$, might be overestimated compared with our value G_2 which was measured directly.

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